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Report on Eu^{3+} and Bi^{3+}/Eu^{3+}-activated phosphors synthesis
WP1 (D1.1)

LEDtech-GROW

LED TECHNOLOGY BASED ON BISMUTH-SENSITIZED Eu^{3+} LUMINESCENCE FOR COST-EFFECTIVE INDOOR PLANT GROWTH

PROGRAM-PROMIS-2024-2025

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Deliverable 1.1

Report on Eu^{3+} and Bi^{3+}/Eu^{3+}-activated phosphors synthesis

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	Abstract: The report includes a description of the synthesis route and a list of prepared traditional Eu^{3+} and Bi^{3+}/Eu^{3+}-activated fluoride phosphors, as well as a novel generation of Eu^{3+} and Bi^{3+}/Eu^{3+}-activated fluoride phosphors. This report is a result of a joint effort between subactivities 1.1 and 1.2. All synthesized phosphors were prepared using green synthesis (HF-free synthesis) via "soft" chemistry routes (coprecipitation, conventional and microwave-assisted hydrothermal techniques).

Document Control Sheet

Document	Title: Report on Eu^{3+} and Bi^{3+}/Eu^{3+}-activated phosphors synthesis.docx
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Executive Summary

The presented document constitutes deliverable D1.1 – *Report on Eu^{3+} and Bi^{3+}/Eu^{3+}-activated phosphors synthesis* of the LEDtech-GROW project. It is a public document, delivered in the context of **WP1** - *Design, synthesis, and characterization of plant-grow-targeted phosphors,* ***Subactivity 1.1*** *- Synthesis and design of traditional Eu^{3+}- and Bi^{3+}/Eu^{3+}-activated inorganic fluoride phosphors [month: 1-12] and* ***Subactivity 1.2 -*** *Synthesis and design of a novel generation of Eu^{3+}- and Bi^{3+}/Eu^{3+}-activated inorganic fluoride phosphors [month: 1-12]*.

This document outlines the detailed synthesis procedure of prepared *Eu^{3+} and Bi^{3+}/Eu^{3+}-activated phosphors* for sharing and disseminating information related to the LEDtech-GROW project. It details the activities, and tools for the synthesis procedure of targeted phosphors, ensuring alignment with both the project objectives and the specific activities of **WP1**.

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Abbreviations and Acronyms

	Explanation
[BYF]	$BaYF_5$
[BGF]	$BaGdF_5$
[DEC]	Dissemination, Communication, and Exploitation
[EDTA-2Na]	Disodium ethylenediaminetetraacetate dihydrate
[LEDtech-GROW]	Acronym of the Project Titled "*LED technology based on bismuth-sensitized* Eu^{3+} *luminescence for cost-effective indoor plant growth*"
[Open Access]	Open access publishing (gold or green open access) means that an article is immediately provided in open-access mode on the publisher or journal's website. Some publishers charge Article Processing Chargers (APCs) to make articles open.
[RYF]	RbY_3F_{10}
[SEF]	Sr_2EuF_7
[SGF]	Sr_2GdF_7
[SGEF]	$Sr_2Gd_{0.2-x}Eu_{0.8}F_7$
[VinaR]	VinaR, i.e. Vinca Repository is a joint digital repository of all laboratories and departments in Vinča Institute of Nuclear Sciences, University of Belgrade. VinaR provides open access to the publications, as well as other outputs of the research projects implemented in these institutions.
[VINS]	"Vinča" Institute of Nuclear Sciences – National Institute of the Republic of Serbia, University of Belgrade
[WP]	Work package

1. Synthesis of Sr_2GdF_7:Eu^{3+} and Sr_2GdF_7:Bi^{3+}, Eu^{3+}

1.1 Synthesis of colloidal and powder Eu^{3+}-doped Sr_2GdF_7 nanoparticles – WP1, sub-activity 1.2

Strontium nitrate ($Sr(NO_3)_2$, Alfa Aesar Karlsruhe, Germany, 99%), gadolinium (III) nitrate hexahydrate ($Gd(NO_3)_3 \cdot 6H_2O$, Alfa Aesar, Karlsruhe, Germany, 99.9%), europium (III) nitrate hexahydrate, ($Eu(NO_3)_3 \cdot 6H_2O$, Alfa Aesar, Karlsruhe, Germany, 99.9%), disodium ethylenediaminetetraacetate dihydrate (EDTA-2Na, $C_{10}H_{14}N_2O_8Na_2 \cdot 2H_2O$, Kemika, Zagreb, Croatia, 99%),), ammonium fluoride (NH_4F, Alfa Aesar, Karlsruhe, Germany, 98%), 25% ammonium solution (NH_4OH, Fisher, Loughborough, Leicestershire, United Kingdom) and deionized water were used as starting materials without further purification.

The hydrothermal method was used to prepare a set of seven $Sr_2Gd_{1-x}Eu_xF_7$ (x = 0, 0.05, 0.10, 0.40, 0.60. 0.80, and 1.00, where mol.% of Eu^{3+} dopant ions were added with respect to Gd^{3+}) colloids, as illustrated in Figure 1. A typical synthesis procedure includes metal nitrates and NH_4F as precursors and EDTA-2Na as a stabilizing agent. Due to the ability to improve crystalline seed dispersibility by forming $[Sr\text{-}EDTA]^{2+}$ and $[Gd\text{-}EDTA]^{+}$ complexes after mixing all the chemicals, EDTA-2Na prevented SGF particle aggregation during the subsequent hydrothermal treatment. At the same time, $[Gd\text{-}EDTA]^{+}$ cations are adsorbed on the surfaces of SGF particles, additionally improving their stability. Typically, for the synthesis, all nitrates were weighed according to the stoichiometric ratio and dissolved in 12.5 ml of deionized water while stirring at room temperature. The solutions were mixed for 30 minutes with a transparent solution of EDTA-2Na in 12.5 ml of water (molar ratio EDTA-2Na:Ln = 1:1). Following that, 10 ml of NH_4F aqueous solution (molar ratio NH_4F:Ln = 12:1) was added and vigorously stirred for 1 hour, yielding a white suspension. The pH value of the mixture was adjusted to around 6 using NH_4OH. Hydrothermal treatment was carried out in a 100-mL Teflon-lined autoclave in the oven at 180 °C for 20 h followed by natural cooling. Obtained colloidal suspensions were acidic with pH = 6. The described method produced undoped SGF and SGF phosphors with varying concentrations of Eu^{3+} ions. The colloidal suspensions were dried in the air, and obtained powders used for XRD analysis, diffuse reflectance, and temperature-dependent photoluminescent measurements. The amounts of precursors used for synthesizing ~0.0025 mol (~1.2 g) of samples are given in Table 1.

Table 1 *The amounts of precursors needed for synthesizing* $Sr_2Gd_{1-x}F_7$:$x$molEu^{3+} *samples.*

Samples	$Sr(NO_3)_2$ (g)	$Gd(NO_3)_3 \cdot 6H_2O$ (g)	$Eu(NO_3)_3 \cdot 6H_2O$ (g)	NH_4F (g)	EDTA (g)
SGF (x=0.00)	1.0582	1.1284	–	1.1111	0.9306
SGF_5Eu (x=0.05)	1.0582	1.0720	0.0557		
SGF_10Eu (x=0.10)	1.0582	1.0156	0.1115		
SGF_40Eu (x=0.40)	1.0582	0.6770	0.4460		
SGF_60Eu (x=0.60)	1.0582	0.4514	0.6690		
SGF_80Eu (x=0.80)	1.0582	0.2257	0.8919		
SEF (x=1.00)	1.0582	–	0.9306		

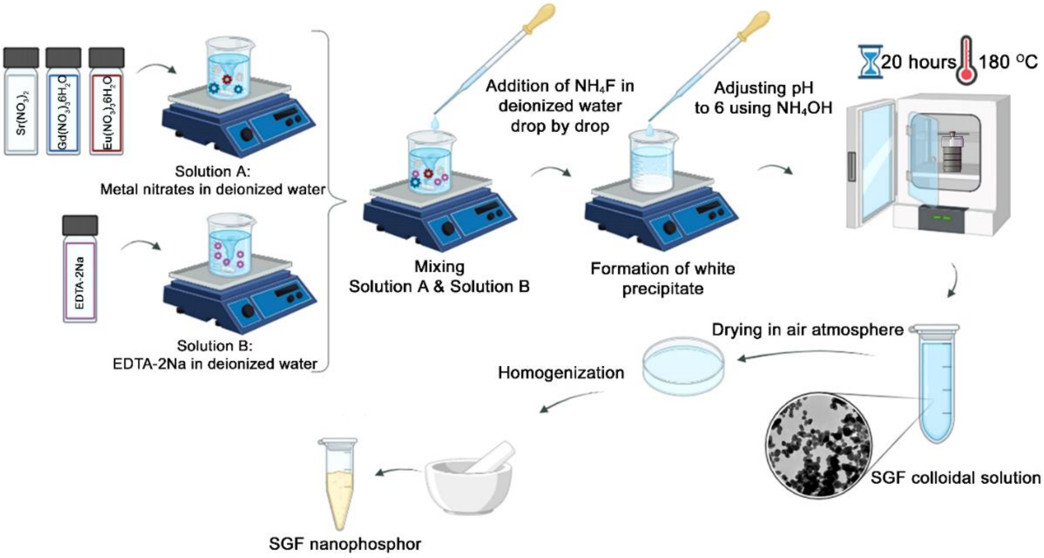

Figure 1. *Schematic illustration of the colloidal and powder SGF:Eu nanophosphors preparation.*

1.2 Synthesis of powder Bi^{3+}-doped Sr_2EuF_7 nanoparticles – WP1, sub-activity 1.2

Synthesis method: The hydrothermal method was used to prepare a set of four $Sr_2Eu_{1-x}Bi_xF_7$ nanoparticles (x = 0.01, 0,02, 0.05, and 0.10 , where mol.% of Bi^{3+} dopant ions were added with respect to Eu^{3+}). A typical synthesis procedure includes metal nitrates and NH_4F as precursors and EDTA as a stabilizing agent. The exact amounts of precursors used for synthesizing ~0.0025 mol of samples are given in Table 2. Hydrothermal treatment was carried out in a 100-mL Teflon-lined autoclave in the oven at 180 °C for 20 h followed by natural cooling.

Table 2 *The amounts of precursors needed for synthesizing $Sr_2Eu_{1-x}F_7$:xmol% Bi^{3+}.*

Samples	$Sr(NO_3)_2$ (g)	$Bi(NO_3)_3$ (g)	$Eu(NO_3)_3\cdot 6H_2O$ (g)	NH_4F (g)	EDTA (g)
SEF_1Bi (x=0.01)	1.0582	0.0099	1.1041	1.1111	0.9306
SEF_2Bi (x=0.02)		0.0197	1.0929		
SEF_5Bi (x=0.05)		0.0494	1.0595		
SEF_10Bi (x=0.10)		0.0988	1.0037		

The synthesis proceeded in several steps:

- Dissolution of $Sr(NO_3)_2$, $Eu(NO_3)_3\cdot 6H_2O$, and $Bi(NO_3)_3$ in 12.5 ml of water with the addition of a small amount of concentrated nitric acid until the solution became completely clear (solution 1), with heating at 60°C.
- Dissolution of EDTA in 12.5 ml of water (solution 2).
- Mixing solution 1 and solution 2, stirring for 30 minutes.
- Dissolution of NH_4F in 10 ml of water (solution 3), dropwise addition of solution 3 to the mixture of solution 1 and 2. After stirring for 15 minutes, the pH is adjusted to 5 with the addition of NH_4OH and stirring for about 1 hour.
- The mixture in the Teflon autoclave is hydrothermally treated in an oven at 180°C for 20 hours.
- After cooling to room temperature, the precipitate is collected by centrifuging at 4000 rpm for 10 minutes, then washed twice with water and water-ethanol mixture (1:1).
- The precipitate is dried at 70°C for several hours.

1.3 Synthesis of powder Bi^{3+}-doped $Sr_2Gd_{0.2}Eu_{0.8}F_7$ nanoparticles – WP1, sub-activity 1.2

Synthesis method: The hydrothermal method was used to prepare a set of five Bi^{3+}-doped $Sr_2Gd_{0.2-x}Eu_{0.8}Bi_xF_7$ nanoparticles (x=0.00, 0.002, 0.01, 0.05, and 0.10 where mol.% of Bi^{3+} dopant ions were added with respect to Gd^{3+}). A typical synthesis procedure includes metal nitrates and NH_4F as precursors and EDTA as a stabilizing agent. The exact amounts of precursors used for synthesizing ~0.0025 mol of samples are given in Table 3. Hydrothermal treatment was carried out in a 100-mL Teflon-lined autoclave in the oven at 180 °C for 20 h followed by natural cooling.

***Table 3** The amounts of precursors needed for synthesizing Bi^{3+}-doped $Sr_2Gd_{0.2-x}Eu_{0.8}F_7$:xmol% Bi^{3+}.*

Samples	$Sr(NO_3)_2$ (g)	$Gd(NO_3)_3·6H_2O$ (g)	$Bi(NO_3)_3$ (g)	$Eu(NO_3)_3·6H_2O$ (g)	NH_4F (g)	EDTA (g)
SGEF_0Bi (x=0.00)	1.0582	0.1947	-	0.8922	1.1111	0.9306
SGEF_0.2Bi (x=0.002)		0.1922	0.0025			
SGEF_1Bi (x=0.01)		0.1849	0.0099			
SGEF_5Bi (x=0.05)		0.1460	0.0494			
SGEF_10Bi (x=0.10)		0.0973	0.0988			

2. Synthesis of $Sr_2LaF_7:Bi^{3+},Eu^{3+}$

2.1 Bi^{3+}-doped Sr_2LaF_7 – WP1, sub-activity 1.2

Synthesis method: The hydrothermal method was used to prepare Bi^{3+}-doped Sr_2LaF_7 nanoparticles (5 mol.% of Bi^{3+} dopant ions were added with respect to La^{3+}). A typical synthesis procedure includes metal nitrates and NH_4F as precursors and EDTA as a stabilizing agent. The exact amounts of precursors used for synthesizing ~0.0025 mol of samples are given in Table 4. Hydrothermal treatment was carried out in a 100-mL Teflon-lined autoclave in the oven at 180 °C for 20 h followed by natural cooling.

***Table 4** The amounts of precursors needed for synthesizing Sr_2LaF_7:5mol%Bi^{3+}.*

Precursors	n [mol]	m [g]
$Sr(NO_3)_2$	0.005	1.05815
$La(NO_3)_3·6H_2O$	0.002375	1.0284
$Bi(NO_3)_3$	0.000125	0.0494
NH_4F	0.03	1.1111
EDTA	0.0025	0.9306

2.2 Bi^{3+}-codoped $Sr_2La_{0.9}Eu_{0.1}F_7$ – WP1, sub-activity 1.2

Synthesis method: The hydrothermal method was used to prepare $Sr_2La_{0.9}Eu_{0.1}F_7$ and Bi^{3+}-codoped $Sr_2La_{0.9}Eu_{0.1}F_7$ nanoparticles (10 mol% of Bi^{3+} dopant ions were added with respect to La^{3+}). A typical synthesis procedure includes metal nitrates and NH_4F as precursors and EDTA as a stabilizing agent. The exact amounts of precursors used for synthesizing ~0.0025 mol of samples are in Tables 5 and 6. Hydrothermal treatment was carried out in a 100-mL Teflon-lined autoclave in the oven at 180 °C for 20 h followed by natural cooling.

***Table* 5** *The amounts of precursors needed for synthesizing $Sr_2La_{0.9}Eu_{0.1}F_7$.*

Precursors	n [mol]	m [g]
$Sr(NO_3)_2$	0.005	1.05815
$La(NO_3)_3{\cdot}6H_2O$	0.00225	0.9743
$Eu(NO_3)_3{\cdot}6H_2O$	0.00025	0.1115
$Bi(NO_3)_3$	-	-
NH_4F	0.03	1.1111
EDTA	0.0025	0.9306

Table 6 *The amounts of precursors needed for synthesizing $Sr_2La_{0.8}Eu_{0.1}Bi_{0.1}F_7$.*

Precursors	n [mol]	m [g]
$Sr(NO_3)_2$	0.005	1.05815
$La(NO_3)_3{\cdot}6H_2O$	0.002	0.8660
$Eu(NO_3)_3{\cdot}6H_2O$	0.00025	0.1115
$Bi(NO_3)_3$	0.00025	0.0988
NH_4F	0.03	1.1111
EDTA	0.0025	0.9306

3. Synthesis of SrF_2:Eu^{3+} and synthesis of SrF_2:Bi^{3+},Eu^{3+}

Synthesis of Eu^{3+}-doped SrF_2 and Bi^{3+}, Eu^{3+}-doped SrF_2 nanoparticles – WP1, sub-activity 1.1

Two sets of samples were synthesized: 1.) SrF_2 doped with different europium ions concentrations: 1, 5, 10, 15, and 20 mol% ($Sr_{1-x}Eu_xF_2$ (x= 0.01, 0.05, 0.1, 0.15, 0.2), Table 7) and 2.) SrF_2 doped with 10 mol% of europium ions and 5, 10, 15, 20, 30, 40 and 50 mol% of bismuth ions ($Sr_{0.9-y}Eu_{0.1}Bi_yF_2$ (y= 0.05, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5), Table 8). Additionally, one more sample, SrF_2 doped with 20 mol% of bismuth ions has been synthesized (SrF_2: 20Bi, exact amounts are given in Table 9).

The chemicals for the synthesis of the desired samples were acquired and used as received: strontium (II) nitrate ($Sr(NO_3)_2$, Alfa Aesar, 99%), europium (III) nitrate hexahydrate ($Eu(NO_3)_3$ x $6H_2O$, Alfa Aesar, 99.9%), bismuth (III) nitrate pentahydrate ($Bi(NO_3)_3$ x $5H_2O$, Sigma Aldrich, 98+%) sodium fluoride (NaF, Alfa Aesar, 99.9%), ethylene glycol (EG) and absolute ethanol (abs. EtOH).

In essence, strontium and europium nitrate in corresponding ratios (for the samples co-doped with bismuth ions, bismuth nitrate was added) were dissolved in ethylene glycol and stirred for 30 minutes. The next step is the addition of an EG solution of sodium fluoride, followed by another 30 minutes of stirring. The precursor mixture was then placed in the microwave reaction vessel and the reaction conditions were a) heating at 150°C for 10 minutes, and b) subsequently cooling to room temperature. The microwave experiments were carried out in an Anton-Paar microwave reactor (Monowave 400) in temperature control mode, utilizing a 30 mL Pyrex jar tightly sealed with a Teflon lid and stirred magnetically at 600 rpm. Each sample obtained through microwave synthesis was transferred into a centrifuge tube, centrifuged, and rinsed several times with abs. EtOH.

Table 7. *Precursors for synthesis of 1 mmol of SrF_2: x mol% Eu^{3+} (x= 1, 5, 10, 15, 20) samples.*

Sample	Abbreviated name	$Sr(NO_3)_2$ (g)	$Eu(NO_3)_3{\cdot}6H_2O$ (g)	NaF (g)	EG (ml)
$\mathbf{Sr_{0.99}Eu_{0.01}F_2}$	SrF_2:1Eu	0.2095	0.00446	0.0840	15
$\mathbf{Sr_{0.95}Eu_{0.05}F_2}$	SrF_2:5Eu	0.2010	0.0223		
$\mathbf{Sr_{0.9}Eu_{0.1}F_2}$	SrF_2:10Eu	0.1905	0.0446		
$\mathbf{Sr_{0.85}Eu_{0.15}F_2}$	SrF_2:15Eu	0.1799	0.0669		
$\mathbf{Sr_{0.8}Eu_{0.2}F_2}$	SrF_2:20Eu	0.1693	0.0892		

Table 8. *Precursors for synthesis of 1 mmol of SrF_2: 10mol% Eu^{3+}, y mol% Bi^{3+} (y= 5, 10, 15, 20, 30, 40, 50) samples.*

Sample	Abbreviated Name	$Sr(NO_3)_2$ (g)	$Eu(NO_3)_3·6H_2O$ (g)	$Bi(NO_3)_3$ x$5H_2O$ (g)	NaF (g)	EG (ml)
$Sr_{0.4}Eu_{0.1}Bi_{0.5}F_2$	SrF_2:10Eu5Bi	0.1799	0.0446	0.0243	0.0840	15
$Sr_{0.8}Eu_{0.1}Bi_{0.1}F_2$	SrF_2:10Eu10Bi	0.1693		0.0485		
$Sr_{0.75}Eu_{0.1}Bi_{0.15}F_2$	SrF_2:10Eu15Bi	0.1587		0.0725		
$Sr_{0.7}Eu_{0.1}Bi_{0.2}F_2$	SrF_2:10Eu20Bi	0.1481		0.0970		
$Sr_{0.6}Eu_{0.1}Bi_{0.3}F_2$	SrF_2:10Eu30Bi	0.1269		0.1455		
$Sr_{0.5}Eu_{0.1}Bi_{0.4}F_2$	SrF_2:10Eu40Bi	0.1058		0.1940		
$Sr_{0.4}Eu_{0.1}Bi_{0.5}F_2$	SrF_2:10Eu50Bi	0.0846		0.2425		

Table 9. *Exact amounts of precursors used for the synthesis of 1mmol of SrF_2:20Bi sample*

Sample	Abbreviated name	$Sr(NO_3)_2$ (g)	$Bi(NO_3)_3·5H_2O$(g)	NaF (g)	EG (ml)
$Sr_{0.8}Bi_{0.2}F_2$	SrF_2:20Bi	0.1693	0.0970	0.0840	15

Figure 2*. Schematic illustration of the precipitation synthesis of SrF_2:Eu,Bi nanoparticles.*

4. Synthesis of BaF_2:Eu^{3+}

Synthesis of Eu^{3+}-doped BaF_2 nanoparticles – WP1, sub-activity 1.1

The chemicals for the synthesis of the desired samples were acquired and used as received: barium (II) nitrate ($Ba(NO_3)_2$, Alfa Aesar, 99%), europium (III) nitrate hexahydrate ($Eu(NO_3)_3$ x $6H_2O$, Alfa Aesar, 99.9%), bismuth (III) nitrate pentahydrate ($Bi(NO_3)_3$ x $5H_2O$, Sigma Aldrich, 98+%) sodium fluoride (NaF, Alfa Aesar, 99.9%), ethylene glycol (EG) and absolute ethanol (abs. EtOH).

In essence, barium and europium nitrate in corresponding ratios (for the samples co-doped with bismuth ions, bismuth nitrate was added) were dissolved in ethylene glycol and stirred for 30 minutes. The next step is the addition of an EG solution of sodium fluoride, followed by another 30 minutes of stirring. The precursor mixture was then placed in the microwave reaction vessel and the reaction conditions were a) heating at 150°C for 10 minutes, and b) subsequently cooling to room temperature. The microwave experiments were carried out in an Anton-Paar microwave reactor (Monowave 400) in temperature control mode, utilizing a 30 mL Pyrex jar tightly sealed with a Teflon lid and stirred magnetically at 600 rpm. Each sample obtained through microwave synthesis was transferred into a centrifuge tube, centrifuged, and rinsed several times with abs. EtOH.). The exact amounts of precursors used for synthesizing are given in Table 10.

Table 10. *Precursors for synthesis of 1 mmol of BaF_2: x mol% Eu^{3+} (x= 1, 5, 10, 15, 20) samples.*

Sample	Abbreviated name	$Ba(NO_3)_2$ (g)	$Eu(NO_3)_3\cdot 6H2O$ (g)	NaF (g)	EG (ml)
$Ba_{0.99}Eu_{0.01}F_2$	BaF_2:1Eu	0.2587	0.0045	0.0840	15
$Ba_{0.95}Eu_{0.05}F_2$	BaF_2:5Eu	0.2483	0.0223		
$Ba_{0.9}Eu_{0.1}F_2$	BaF_2:10Eu	0.2352	0.0446		
$Ba_{0.85}Eu_{0.15}F_2$	BaF_2:15Eu	0.2221	0.0669		
$Ba_{0.8}Eu_{0.2}F_2$	BaF_2:20Eu	0.2091	0.0892		

5. Synthesis of $BaYF_5:Eu^{3+}$ and $BaYF_5:Bi^{3+},Eu^{3+}$

Synthesis of Eu^{3+}-doped $BaYF_5$ and Bi^{3+}, Eu^{3+}-doped $BaYF_5$ nanoparticles – WP1, sub-activity 1.2

Yttrium(III) nitrate hexahydrate ($Y(NO_3)_3\cdot 6H_2O$, 99.8%) was purchased from Aldrich, while bismuth(III) nitrate pentahydrate ($Bi(NO_3)_3\cdot 5H_2O$, 98.0%) was from Reanal. Europium(III) nitrate hexahydrate ($Eu(NO_3)_3\cdot 6H_2O$, 99.9%), barium nitrate ($Ba(NO_3)_2$, 99.95%) and ammonium fluoride (NH_4F, 98%) were obtained from Alfa Aesar. Glycerol (≥99%) was purchased from Acros Organics. All the materials were used without further purification.

Three sets of nanophosphors were synthesized using the solvothermal method: 1. $BaYF_5$: xEu, where $x = 1, 10, 20$ mol%; 2. $BaYF_5$: 10Eu, yBi, where $y = 0, 5, 10, 20, 30, 50$ mol%; and 3. $BaYF_5$: xEu, 20Bi where $x = 1, 5, 10, 20$ mol%. Each synthesis was conducted through the steps presented in Figure 3. Initially, $Ba(NO_3)_2$, Ln-nitrates, and $Bi(NO_3)_3$ were weighted according to the stoichiometric ratio (nominal amounts in precursor mixture are presented in Table 11) and dissolved in 7.0 ml water and 7.5 ml glycerol. After that, an excess amount of NH_4F was dissolved in 1.0 ml water and added dropwise to the initial solution. The resulting solution was maintained with a strong stirring for 1 h at room temperature. This mixture was then transferred into a 50-mL Teflon-lined autoclave and heated in the oven at 180°C for 21 h. The obtained nanoparticles were centrifuged at 4000 rpm for 10 minutes, washed in water and ethanol:water = 1:1 mixture, and air dried before further characterization.

Table 11. *The final precursor quantities for the synthesis of the representative BYF:10Eu, yBi (y = 0, 5, 10, 20, 30, 50 mol%) sample set.*

Bi^{3+} (mol%)	$Ba(NO_3)_2$ (mmol)	$Y(NO_3)_3\cdot 6H_2O$ (mmol)	$Eu(NO_3)_3\cdot 6H_2O$ (mmol)	$Bi(NO_3)_3$ (mmol)	NH_4F (mmol)
0	1.00	0.90	0.10	/	7.00
5		0.85		0.05	
10		0.80		0.10	
20		0.70		0.20	
30		0.60		0.30	
50		0.40		0.50	

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LED technology based on bismuth-sensitized Eu^{3+} luminescence for cost-effective indoor plant growth – LEDtech-GROW

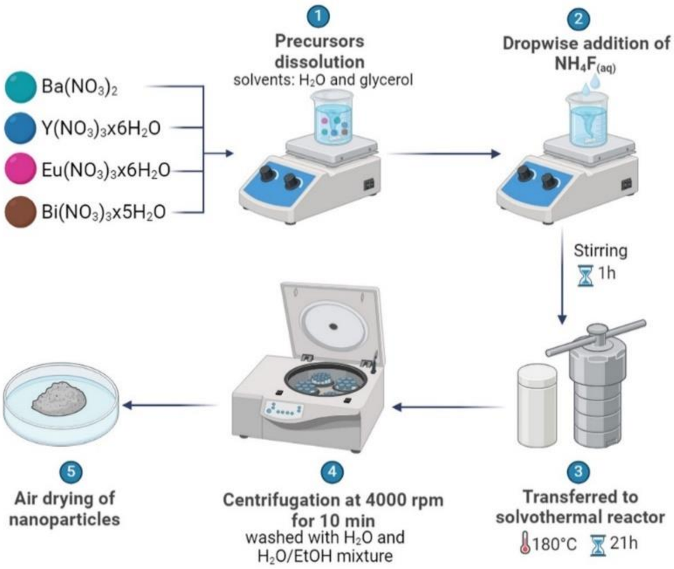

***Figure 3**. Schematic illustration of the solvothermal synthesis of BYF: Eu, Bi nanoparticles. The precursors were initially dissolved in a water-glycerol mixture and fluoride ions were added dropwise (steps 1, 2). After vigorous stirring, the resulting mixture was transferred to a Teflon-lined autoclave and heated to 180°C for 21 h (step 3). The resulting nanoparticles were subsequently washed, centrifuged, and left to dry in air (steps 4, 5).*

6. Synthesis of $BaGdF_5:Eu^{3+}$, $BaGdF_5:Bi^{3+},Eu^{3+}$

Synthesis of Eu^{3+}-doped $BaGdF_5$ and Bi^{3+}, Eu^{3+}-doped $BaGdF_5$ nanoparticles – WP1, sub-activity 1.2

The synthesis was conducted through the steps presented in Figure 3. Initially, $Ba(NO_3)_2$, Ln-nitrates, and $Bi(NO_3)_3$ were weighted according to the stoichiometric ratio (nominal amounts in precursor mixture are presented in Table 12) and dissolved in 7.0 ml water and 7.5 ml glycerol. After that, an excess amount of NH_4F was dissolved in 1.0 ml water and added dropwise to the initial solution. The resulting solution was maintained with a strong stirring for 1 h at room temperature. This mixture was then transferred into a 50-mL Teflon-lined autoclave and heated in the oven at 180°C for 21 h. The obtained nanoparticles were centrifuged at 4000 rpm for 10 minutes, washed in water and ethanol:water = 1:1 mixture, and air dried before further characterization. Future work will focus on the optimization of Eu content in BGF, and Bi^{3+}-co-doping the representative BGF:Eu nanophosphor.

***Table 12.** Precursors for synthesis of $BaGdF_5$: 10 mol% Eu^{3+} sample.*

$BaGdF_5$	**$Ba(NO_3)_2$ (g)**	**$Gd(NO_3)_3 \cdot 6H_2O$ (g)**	**$Eu(NO_3)_2 \cdot H_2O$ (g)**	**NH_4F (g)**
BGF:10Eu	0.2570	0.4059	0.0447	0.2590

7. Synthesis of RbY_3F_{10}:Eu^{3+}

Synthesis of Eu^{3+}-doped RbY_3F_{10} nanoparticles – WP1, sub-activity 1.2

Using the microwave-assisted solvothermal method, we synthesized the fluoride host material RbY_3F_{10} doped with Eu^{3+}. By varying the chelating agents (EDTA, Na_2EDTA, citric acid) and pH we controlled the coordination environment around the metal ions, resulting in different products. The exact amounts of precursors used for synthesizing are given in Table 13.

Table 13. Precursors for the synthesis of RbY_3F_{10}: x mol% Eu^{3+} sample.

RbY_3F_{10}	RbF (g)	Y_2O_3 (g)	$Eu(NO_3)_3·6H_2O$ (g)	NH_4F(g)	EDTA(g)	Citric acid(g)
RYF:10Eu_1	0.0522	0.1525	0.0670	0.1850	/	0.2880
RYF:10Eu_2					/	/
RYF:10Eu_3					0.4384	
RYF:10Eu_4					0.0730	
RYF:1Eu		0.1678	0.0067			
RYF:5Eu		0.1610	0.0335			
RYF:15Eu		0.1441	0.1006			
RYF:30Eu		0.1186	0.2010			
RYF:50Eu		0.0847	0.3350			

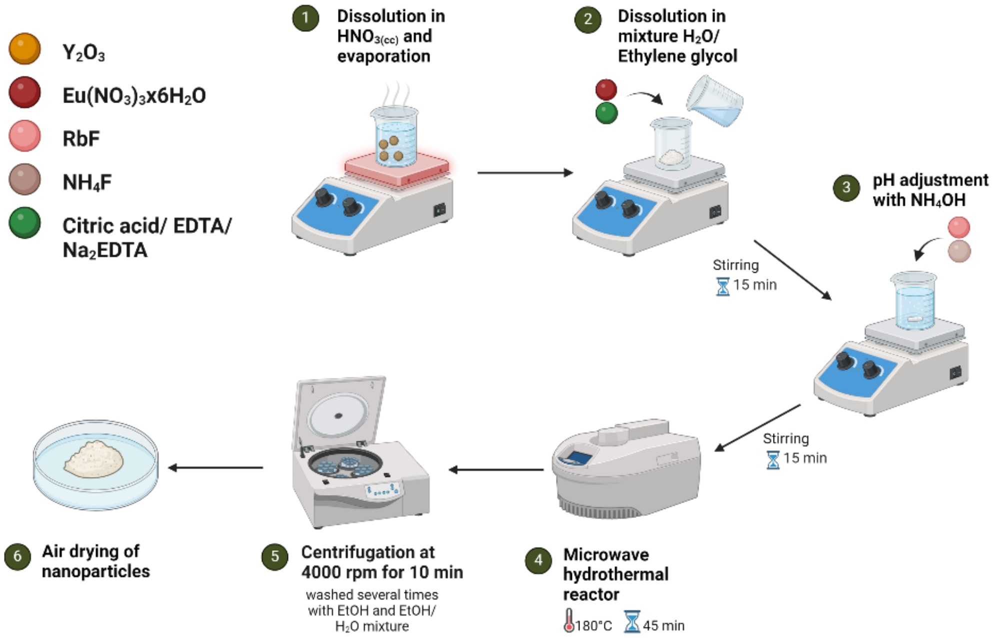

Figure 4. Schematic illustration of the solvothermal synthesis of RbY_3F_{10}: Eu nanoparticles.

8. Synthesis of $GdF_3:Eu^{3+}$, $GdF_3:Bi^{3+},Eu^{3+}$

Synthesis of Eu^{3+}-doped GdF_3 nanoparticles – WP1, sub-activity 1.1

Using the coprecipitation method, we synthesized the fluoride host material $GdF_3:Eu^{3+}$. By varying the annealing temperature (400°C (2h), 500°C (2h), 600°C (2h), and 500°C (5h)) we controlled the crystallinity of the products. The exact amounts of precursors used for the synthesis of GdF_3: 10 mol% Eu^{3+} samples are given in Table 14. Future work will focus on optimization of Eu^{3+} content in GdF_3, and Bi^{3+}-co-doping of representative GdF_3:Eu nanophosphors.

Synthesis:

- Dissolving rare earth nitrates in 8 ml distilled water and 4 ml ethylene glycol (solution A).
- Dissolving NH_4F in 8 ml distilled water and 4 ml ethylene glycol (solution B).
- Stirring solutions A and B for 2 hours
- Washing the previously centrifugated precipitates several times with H_2O: EtOH = 1:1
- Drying overnight and then annealing at different temperatures.

Table 13. *Precursors for the synthesis of GdF_3: 10 mol% Eu^{3+} samples.*

GdF_3	$Gd(NO_3)_3\cdot6H_2O$ (g)	$Eu(NO_3)_2\cdot5H_2O$ (g)	NH_4F (g)
10 mol.% Eu	1.6248	0.1784	0.4444

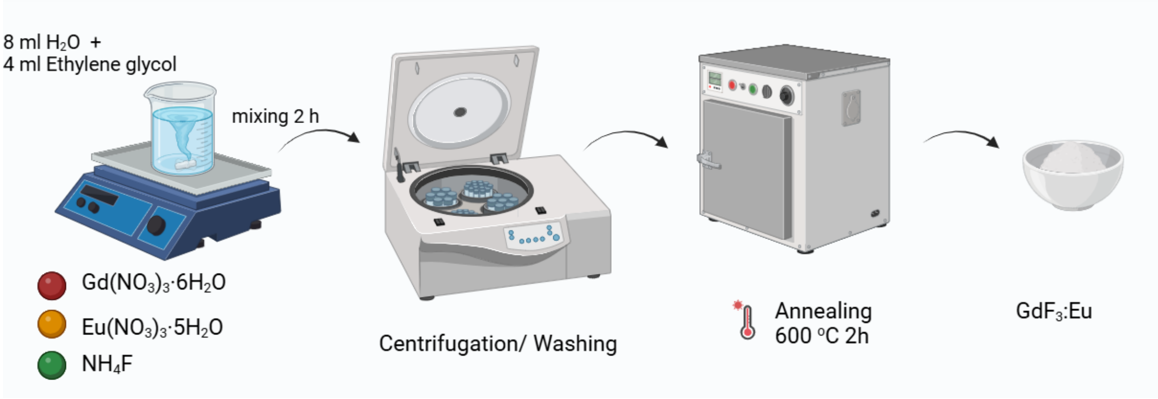

Figure 5*. Schematic illustration of the precipitation synthesis of GdF_3:Eu nanoparticles.*

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LED technology based on bismuth-sensitized Eu^{3+} luminescence for cost-effective indoor plant growth – LEDtech-GROW

9. Scientific Publications and Peer-Reviewed Journals

During the first year of the project implementation, the LEDtech-GROW team achieved the following: three papers were published in peer-reviewed journals, all of which are Open Access as per the grant agreement; four poster presentations were delivered at international conferences; and one invited talk was given at a domestic conference.

1. B. Milićević, A. Ćirić, Z. Ristić, M. Medić, A. N. Alodhayb, I. Radosavljević Evans, Ž. Antić, M. D. Dramićanin. "*Eu3+- activated Sr2GdF7 colloid and nano-powder for horticulture LED applications". Journal of Alloys and Compounds 1010 (5) (2025) 177820. https://doi.org/10.1016/j.jallcom.2024.177820*
2. K. Milenković, Lj. Đačanin Far, S. Kuzman, Ž. Antić, A. Ćirić, M. D. Dramićanin, B. Milićević. "Red emission enhancement in BaYF$_5$:Eu^{3+} phosphor nanoparticles by Bi^{3+} co-doping*". Optics Express* 32 (23) (2024) 41632-41643 https://doi.org/10.1364/OE.542685
3. J. Periša, S. Kuzman, A. Ćirić, Z. Ristić, Ž. Antić, M. D. Dramićanin, B. Milićević. "Tuneable Red and Blue Emission of Bi^{3+}-Co-Doped SrF$_2$:Eu^{3+} Nanophosphors for LEDs in Agricultural Applications". *Nanomaterials* 14(20), 1617. https://doi.org/10.3390/nano14201617
4. K. Milenković, V. Đorđević, I. Zeković, Z. Ristić, J. Periša, B. Milićević, M. D. Dramićanin: "Microwave-assisted solvothermal method for RbY$_3$F$_{10}$ doped with Eu^{3+}"- The 7th International Conference on the Physics of Optical Materials and Devices & The 4th International Conference on Phosphor Thermometry (ICOM&ICPT 2024), August 26-30, 2024, Bečići, Budva Montenegro, P-50, (pp 165).
5. S. Kuzman, B. Milićević, J. Periša, A. Ćirić, Z. Ristić, Ž. Antić, M. D. Dramićanin: "Synthesis and photoluminescent properties of Bi^{3+}-codoped SrF$_2$:Eu^{3+} phosphor nanoparticles"- The 7th International Conference on the Physics of Optical Materials and Devices & The 4th International Conference on Phosphor Thermometry (ICOM&ICPT 2024), August 26-30, 2024, Bečići, Budva Montenegro, P-51, (pp 166).
6. B. Milićević, A. Ćirić, Z. Ristić, M. Medić, I. Radosavljevic Evans, Ž. Antić, M. D. Dramićanin: "Synthesis, luminescent properties, and thermal stability of Eu^{3+}-doped Sr$_2$GdF$_7$ red-emitting nanophosphor for horticulture LEDs"- The 7th International Conference on the Physics of Optical Materials and Devices & The 4th International Conference on Phosphor Thermometry (ICOM&ICPT 2024), August 26-30, 2024, Bečići, Budva Montenegro, P-53, (pp 168).
7. K. Milenković, V. Đorđević, S. Kuzman, J. Periša, B. Milićević, Miroslav D. Dramićanin: "Three-fold enhancement of Eu^{3+} emission intensity in BaYF$_5$ nanoparticles by Bi^{3+} co-doping", -12th International Conference on Luminescent Detectors and Transformers of Ionizing Radiation (LUMDETR), June 16-21, 2024, Riga, Latvia, PA13, (pp 89).
8. S. Kuzman, B. Milićević, K. Milenković, J. Periša, M. D. Dramićanin: "Bizmuth-sensitized Eu^{3+} luminescent LED technology for effective indoor plant growth"- The 3rd Serbian Conference on Materials Application and Technology (SCOM2024), October 16-18, Belgrade, Serbia, I-1, (pp 8). *Invited talk*

LEDtech-GROW team members reached **Milestone M1.1 - A list of Eu^{3+} and Bi^{3+}/Eu^{3+}-activated phosphors defined** (verification: Single-phase crystal structure and appropriate phosphors' emission that matches the PAR spectrum). The list is as follows:

1. Eu^{3+}-doped Sr_2GdF_7 colloidal and powder nanoparticles

2. Eu^{3+}-doped RbY_3F_{10} powder nanoparticles

3. Bi^{3+}, Eu^{3+}-doped SrF_2 nanopowders

4. Bi^{3+}, Eu^{3+}-doped $BaYF_5$ powder nanoparticles